

CHAPTER 3

THEORY

Production of Petroleum Base Oils

Lubricating oils are generally manufactured from petroleum base oils according to the following steps.

1. Distillation, to adjust the viscosity and flash point
2. Refining, to improve the oxidation stability and viscosity-temperature characteristics.
3. Deasphalting of the residue from vacuum distillation.
4. Dewaxing to improve the low-temperature properties.
5. Blending of base oils and additives, to make lubricating oils with specific properties depending on their applications.

In the early history, simple distillation was used to recover the lower boiling gasoline and kerosine fraction and leave a residue which was used as lubricant. It was also found that removing of some components could improve the quality of the petroleum base oils. These components are asphalt, aromatic, wax, etc. Asphalt was removed from distillates from atmospheric distillation by vacuum distillation. Wax was removed by chilling the lube distillate and filtering in plate and frame processes. Aromatics were reduced by treating the oil with sulphuric acid and separating the acid tar phase. Final step called finishing process was used to remove acid residue and impurities which gave further improvement in product quality. At that time, most of processes were batch operations. Therefore, there were not suitable for the large expansion in production capacity.

In last 30 years new technology has been developed. Catalytic hydrogenation have become the normal method for finishing of base oils and it is the alternative method to solvent extraction in reducing the aromatic content in oils. Figure 3-1 shows the simplified refinery flow-scheme which we can see where lubricant base oil plant fit in. Figure 3-2 shows steps of base oils production starting from vacuum distillation column which is fed with atmospheric residue. Distillates and residue from vacuum distillation are separated by mean of their different boiling range. Then, They are sent to the other processes such as deasphalting, extraction, dewaxing and finishing. These process are explained in the next section.

1. Distillation

Fractional distillation of lubricating base oils, the residue from the atmospheric is transferred directly to a vacuum distillation column where it is

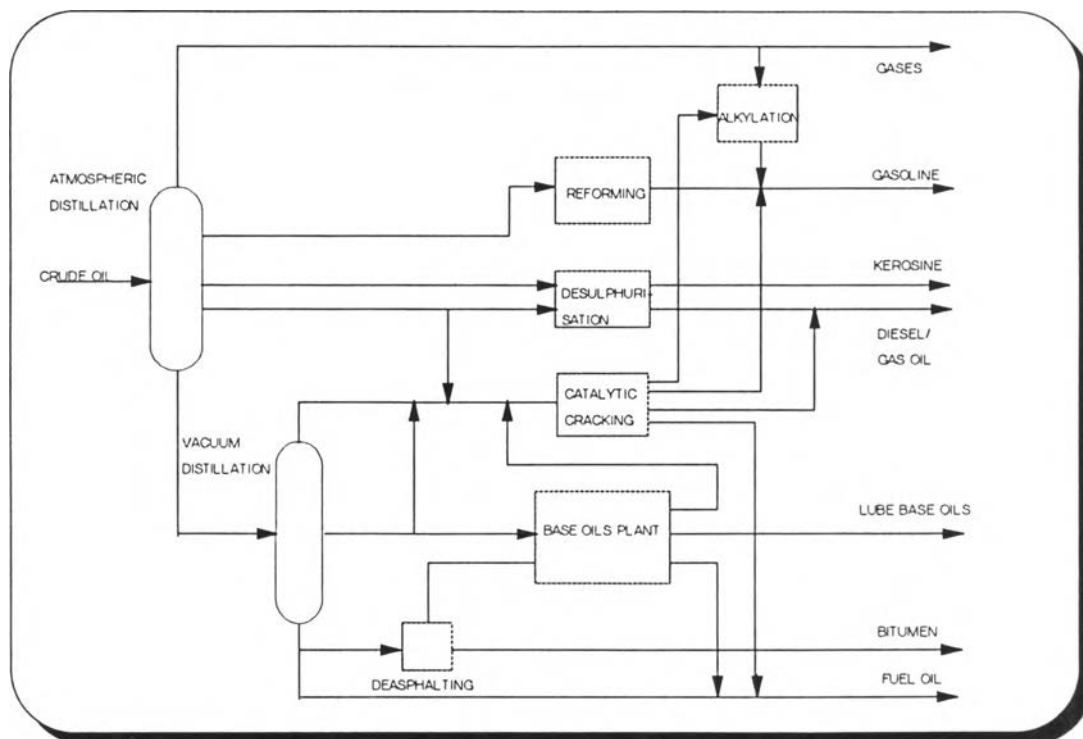


Fig. 3.1 Simplified refinery flow-scheme

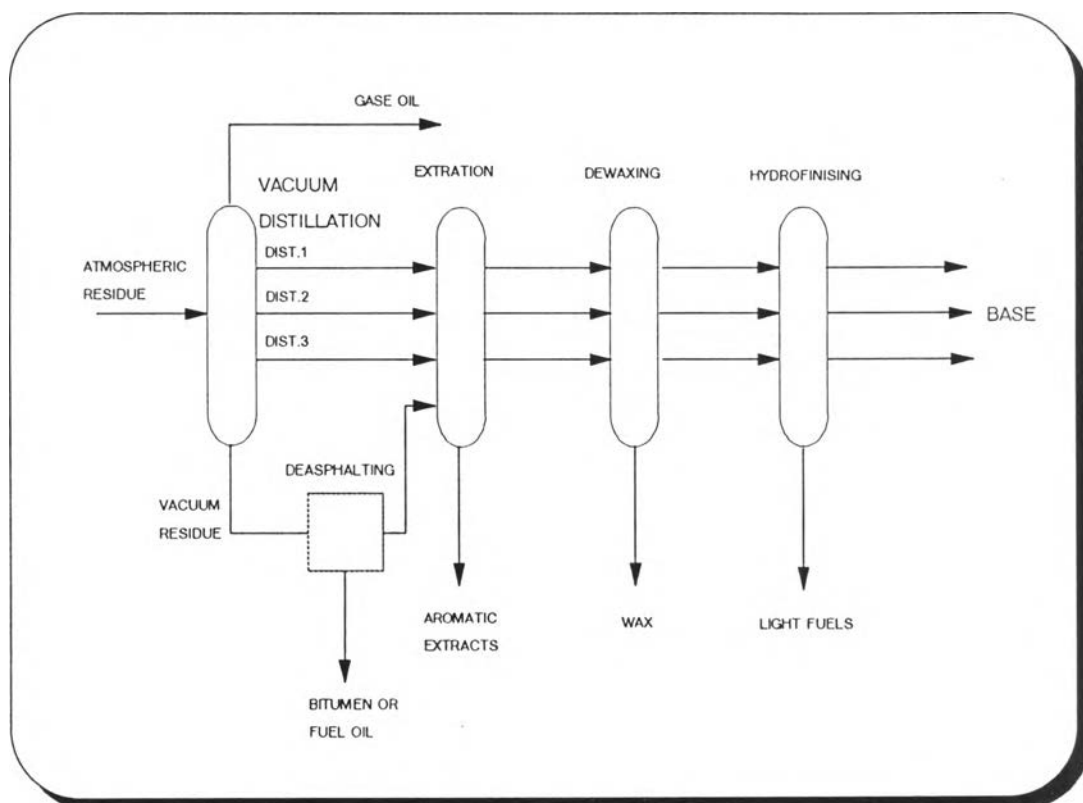


Fig. 3.2 Base oil production flow-scheme

separated into different lube oil cut and the residue. The purpose of distillation is to adjust the flash point and viscosity of oils. The flash point of a fraction depends on the low boiling components, even if they present only in small quantities. It also depends on the fractionation efficiency of the distillation column which can be improved by stripping with steam in auxiliary columns.

The viscosity is a function of the boiling range and thus of molecular mass. In the vacuum distillation viscosity is the determining parameter if adjustment of the boiling range is difficult. Figure 3.3 shows the production of individual fractions from a naphthenic crude and their typical data are given in table 3.1

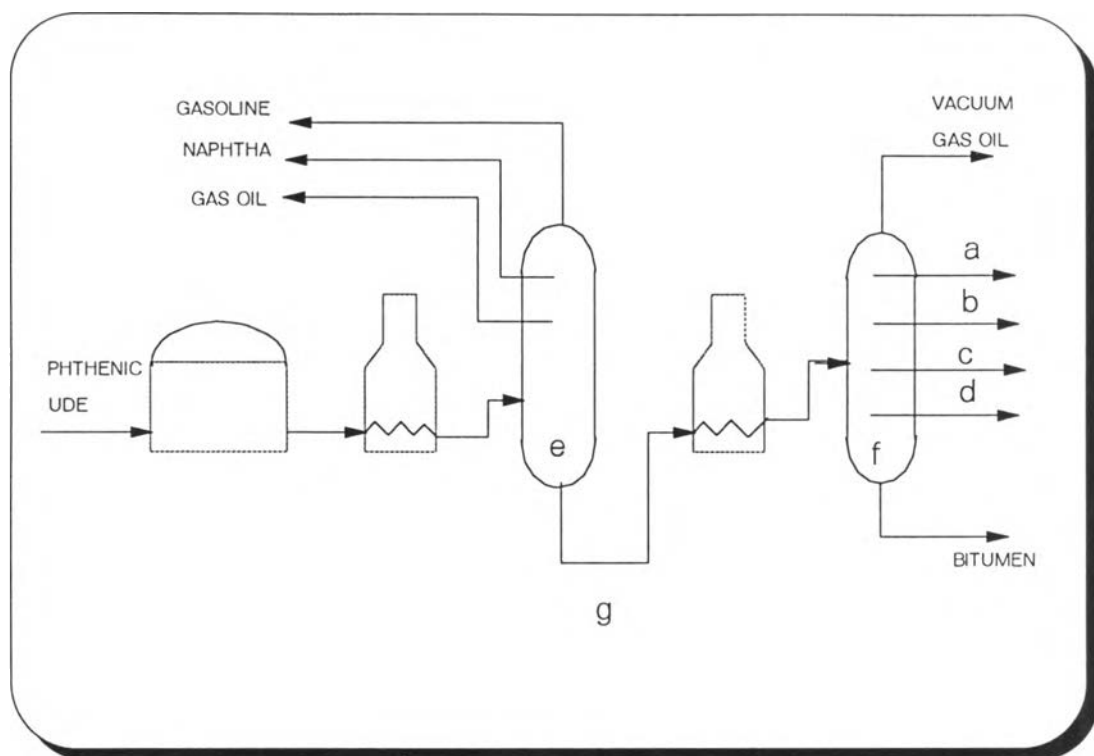


Fig. 3.3 Distillation unit for the production of four lube oil cuts from naphthenic crude oil a light spindle oil; b heavy spindle oil; c light lube oil; d heavy lube oil; e atmospheric column; f vacuum column; g atmospheric residue.

Table 3.1 Typical properties of lubrication Oil Fractions from a Naphthenic Crude

| | Feed | Light Spindle oil | Heavy Spindle oil | Light Lube oil | heavy Lube oil | Vacuum Residue |
|------------------------------|-------|-------------------|-------------------|----------------|----------------|----------------|
| Density at 15 C, g/ml | 0.949 | 0.900 | 0.915 | 0.930 | 0.936 | 1.017 |
| Viscosity at 40 C, cSt. | 371 | 10.1 | 26.6 | 119 | 380 | - |
| Viscosity at 100 C, cSt. | 21.8 | 2.48 | 4.25 | 9.73 | 19.5 | 3100 |
| Viscosity Index | 65 | 52 | 28 | 36 | 37 | - |
| Flash point , C | 203 | 160 | 181 | 221 | 258 | 338 |
| Penetration at 25 C, 1/10 mm | | | | | | 110 |
| Softening point , C | | | | | | 45 |

2. Refining

The vacuum distillates contain undesirable components which lead to darkening, viscosity increases and the formation acid and sludge even after a short service time of oil. Removal of these components, i.e. Olefins formed due to overheating on the hot tube in distillation column, by refining makes it possible to produce high quality base oils from crudes which were originally unsuited for this purpose. Three different refining processes are available:

Acid refining and separation of the acid tar formed;
Extraction with selective solvents (Solvent Extraction);
Catalytic hydrogenation (hydrotreating).

The advantage of these procedure is that the improve the aging stability and the VT characteristics. Refining removes also compounds such as sulfur- containing heterocycle which act as natural oxidation inhibitor. Table 3.2 shows undesirable components in lube base oil and methods of removal.

2.1 Acid refining

This is the classical refining process which sulfuric acid or oleum (fuming sulfuric acid) is used to treat lube oil distillates. Even this are being replac- ed by modern processes, many plants of this type are still in

operation. Besides improving the color, the color stability and aging tendency, the treatment has also improved the other properties. However, poor selectivity and acid waste from the process are the important disadvantages of this process.

Table 3.2 Undesireable components of Lube oil Fractions.

| components | Effect | Removed by |
|---|--|----------------------------|
| Acid, e.g. naphthenic acid | Reduced storage stability Corrosion hazard | Refining |
| Sulfur Compounds | Reduced storage stability Corrosivity Unpleasant smell | Refining |
| Unstable (extractable) Compounds, such as olefins unstable aromatics nitrogen compounds | Reduced storage stability | Refining |
| Asphaltness and resins | sludge formation | Refining |
| Paraffin wax | Poor flow properties at low temperature | Selective Precipitation |

In dry refining process, concentrated sulfuric acid is used to convert unstable components (particularly olefins) to sulfonates or polymeric products which are insoluble in the oil and thus can be separated. The black, tar-like polymerizates are precipitated together with excess sulfuric acid. Product from this process contains small amounts of dissolved acid resins and traces of sulfuric acid; it is therefore treated simultaneously with calcium hydroxide and adsorbent (mostly bleaching clay). The spent bleaching clay and calcium sulfate are then separated by filtration. The product obtained is neutral and has light color. Normally, acid used in treatment is less than 10% mass.

For Oleum refining (Wet refining), fuming sulfuric acid must be used in order to obtain aging resistant oils or oils with low aromatics content. The olefins and aromatics in oil are slowly reacted with free sulfur trioxide and formed sulfuric acid esters and sulfonic acids. Saturated paraffins and cycloparaffinic hydrocarbons also react with sulfur trioxide, thus leading to refining losses. The reaction products are separated together with unreacted acid in the form of a black, high viscous acid tar. An aqueous solution of caustic alkali is used to neutral naphthasulfonic acid and then extracted with alkanols. The following process is bleaching of oil with bleaching clay. With the large amount of oleum (up to 100 mass % related to the oil), olefins and aromatics are removed practically completely and white oils without color, smell and taste are obtained.

The treatment temperature of acid refining process must be kept as low as possible since at low temperature the reactions proceed at a lower rate and are easier to control. Moreover, the selectivity is better at low temperature. The treatment time is approximately equal in all case (20–40 min). Acid refining is either carried out in a batch-wise operation in mixing tank or continuously in a mixing pump. Figure 3.4 and 3.5 show the batch and continuous acid refining respectively.

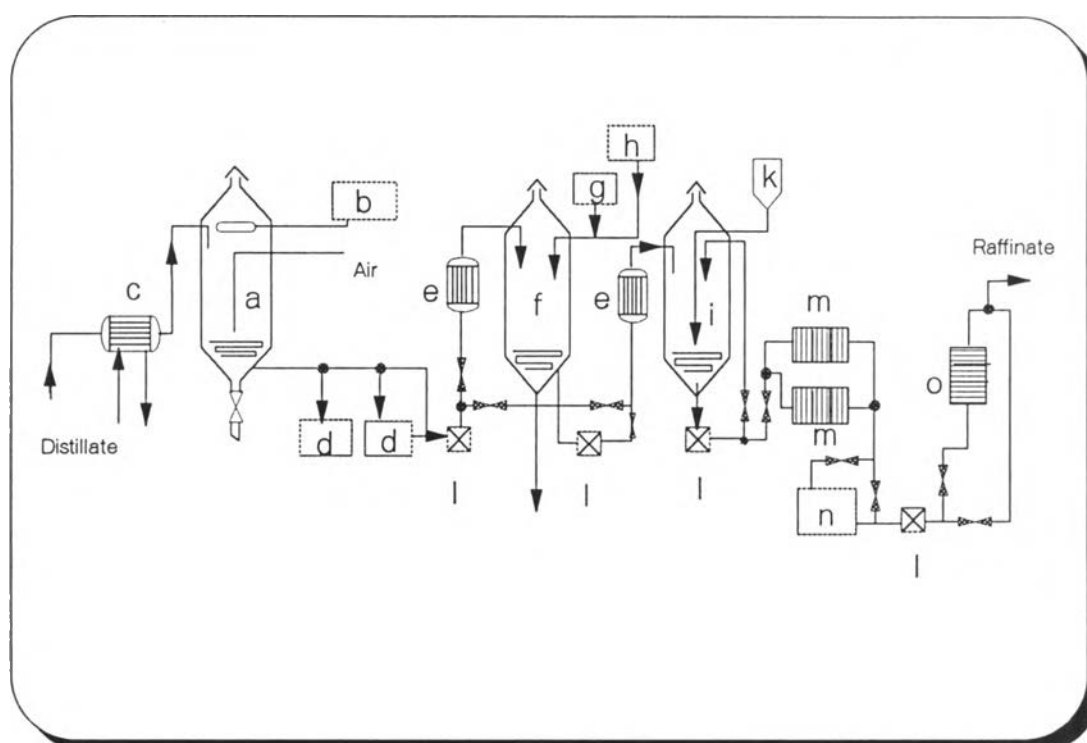


Figure 3.4 Batch acid refining

- a. Acid agitator; b. acid dosage vessel; c. cooler or preheater; d. intermediate trough for sour oil;
- e. preheater; f. neutralization agitator; g. dosage

vessel for alcoholic alkali; h. dosage vessel for wash alcohol, i. bleaching clay agitator; k. hopper and dosage vessel for bleaching clay and calcium hydroxide; l. filtering and circulating pumps; m. main filter presses; n. intermediate raffinate storage vessel; o. final filter press.

2.2 Solvent Refining

Solvent refining or solvent extraction is the term for the removal of aromatics and other undesirable substances of lubricating base oil distillate by liquid-liquid extraction. Suitable extractants (solvents) are phenol, furfural, sulfur dioxide, and N-methylpyrrolidone (NMP). Aniline, nitrobenzene and chlorex have lost in significance.

In 1912 B. Edeleanu found that aromatics are easily soluble in liquid sulfur dioxide, while the solubility of naphthenes and paraffins is poor. Therefore, the first refining process was based on solvent extraction. This basis has been used for all extraction processes which different solvents are used in stead of sulfur dioxide.

In most cases the viscosity index or viscosity density constant are the critical criteria which determine the extraction condition, not the aromatics content itself. For economic reasons, the extraction is carried out only to the highest permissible aromatics content of the raffinate. Besides improving the aging stability, solvent extraction reduces the density and viscosity of the raffinates in comparison with the distillates. The viscosity index increases with the amount of separated extract. The treatment has no significant effect on the flash point but significantly improve the carbon residue, color, color stability. The sulfur content is reduced about 50 %, depending on the origin of oil.

Solvent Extraction with Sulfur dioxide. Sulfur dioxide was the first selective solvent to be used on a large scale. However, its relatively low selectivity is the major problem of this process. Moreover, strongly corroding sulfurous acid is formed if sulfur dioxide contact with water. Before processing, Contaminated water in oil must be removed in drying equipment to less than 0.005 mass %. The oil is then cooled by liquid sulfur dioxide and transferred to the extraction tower where aromatics, olefins and a part of sulfur compounds are extracted counter-currently with liquid sulfur dioxide. The extract containing most of the sulfur dioxide is drawn off from the bottom, the raffinate at the top of the tower.

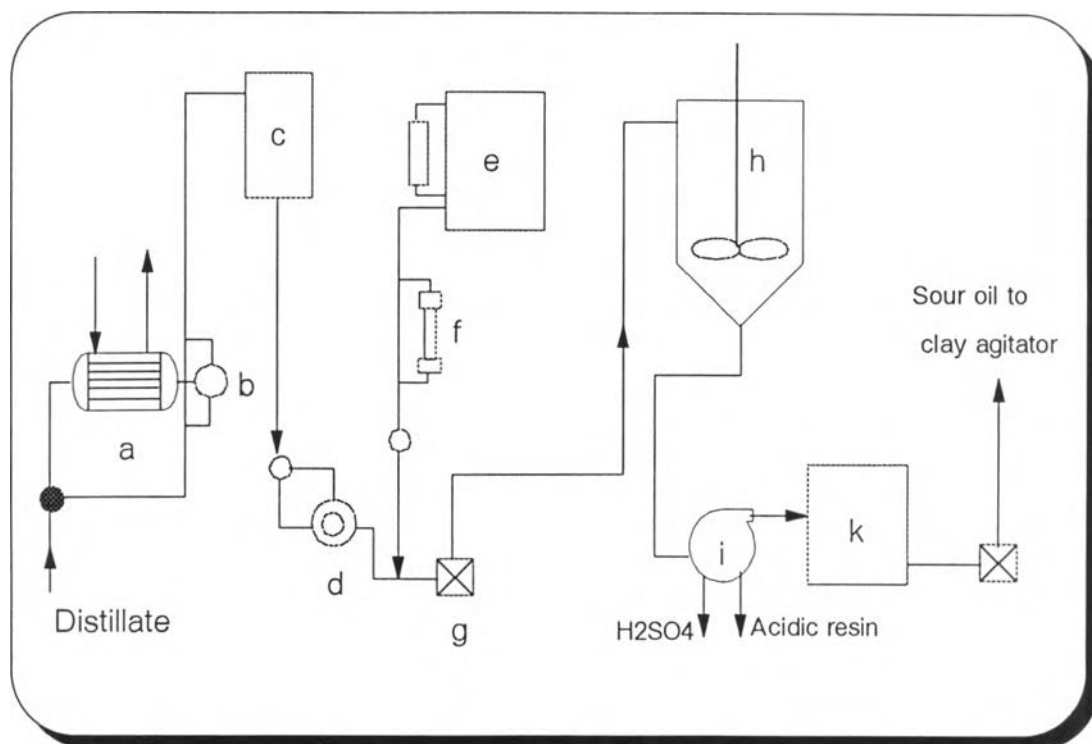


Figure 3.5 Continuous acid refining

- a. Distillate preheater; b. temperature control;
- c. distillate working tanks; d. distillate flow control;
- e. acid container; f. acid flow control; g. mixing pump;
- h. reactor; i. centrifuge; k. sour oil collector.

Solvent Extraction with Furfural. Furfural is widely used as extractant due to better selectivity over sulfur dioxide and which decrease less rapidly with increasing temperature than the selectivity of other extractants. Therefore, it can be used for the refining of high pour point oils where high operating temperature is required. It is a particularly good solvent for constituents of the distillates which are susceptible to oxidation and which contribute most to the sludge and coke forming tendency of oils. It is also a good solvent for strongly colored constituents, as well as for resins and sulfur compound. Furfural is non-corrosive even in aqueous solutions.

Solvent Extraction with Phenol. The extraction Characteristics of phenol are similar to those of furfural. Its selectivity depends on the water content. In phenol extraction the feedstock is passed first through an absorption tower to recover trace of phenol from the waste stream of the unit and proceeds then to the centrifugal extractor. Phenol is removed from raffinate by evaporation and subsequent stripping with steam. The extract phase is transferred from the centrifugal extractor through a heater to the drying tower in which water is removed. The water-free solution is

transferred from the sump of the drying tower to the extract flash tower in which most of phenol is vaporized. The last traces of phenol are removed from the remaining extract with steam in the extract stripper.

Solvent Extraction with N-Methyl-2-Pyrrolidone (NMP). NMP is a highly selective non-toxic solvent which has been used for solvent extraction of lubricating oil distillates and brightstock. Its high selectivity makes it possible to convert low quality distillates to high quality lubricating oil. A low solvent-to-oil ratio is sufficient, so that investment and operating cost can be saved. Existing extraction units can be converted to NMP. An NMP extraction plant consists of the extraction unit, the unit for the stripping of NMP from the raffinate and extract phases, and the NMP drying unit.

2.3 Catalytic Hydrogenation

Catalytic hydrogenation (hydrotreating) removes or transforms undesirable impurities from petroleum distillates. The aromatics are hydrogenated to a large or lesser degree depending on how the reaction is conducted. Hydrotreating is the most favorable method among the refining processes due to the small material losses involved. Three types of hydrotreating are described as followings.

Hydrofinishing is a mild hydrotreating which is usually applied as the final step after solvent refining in order to remove remaining traces of undesirable compounds replacing mild sulfuric acid or clay aftertreatment which were formerly in use. Hydrofinishing is a refining hydrogenation carried out to improve the color, odor, stability and demulsibility properties of lubricating oil distillates. The after treatment of solvent raffinates is sometime also called hydrofining. High-pressure hydrogenation provides complete removal of the heterocompounds, a nearly complete hydrogenation or hydrodecyclisation of the aromatic ringcompounds and a hydroisomerisation of n-paraffins into isoparaffins.

There is no specific designed for only one of the three types above. For one specific plant, process parameters, such as pressure, temperature and space velocity, may be varied to cover several duties. The principle of lube oil hydrotreating, the oil feed is preheated to temperature between 150 C. and 420 C. and then run together with hydrogen or a hydrogen-enriched gas, respectively, through a fixed bed reactor. The oil react with the hydrogen in the presence of a catalyst which is based on regenerable metal oxides. Process is operated at pressure between 14 and 100 bar or even up to 170 bar if high pressure hydrogenation is applied. The product leaving reactor is then cooled before separation of

ed more and more by hydrotreating, it is still important for special product as the last stage in lubricating oil processing which removes the last traces of undesirable impurities.

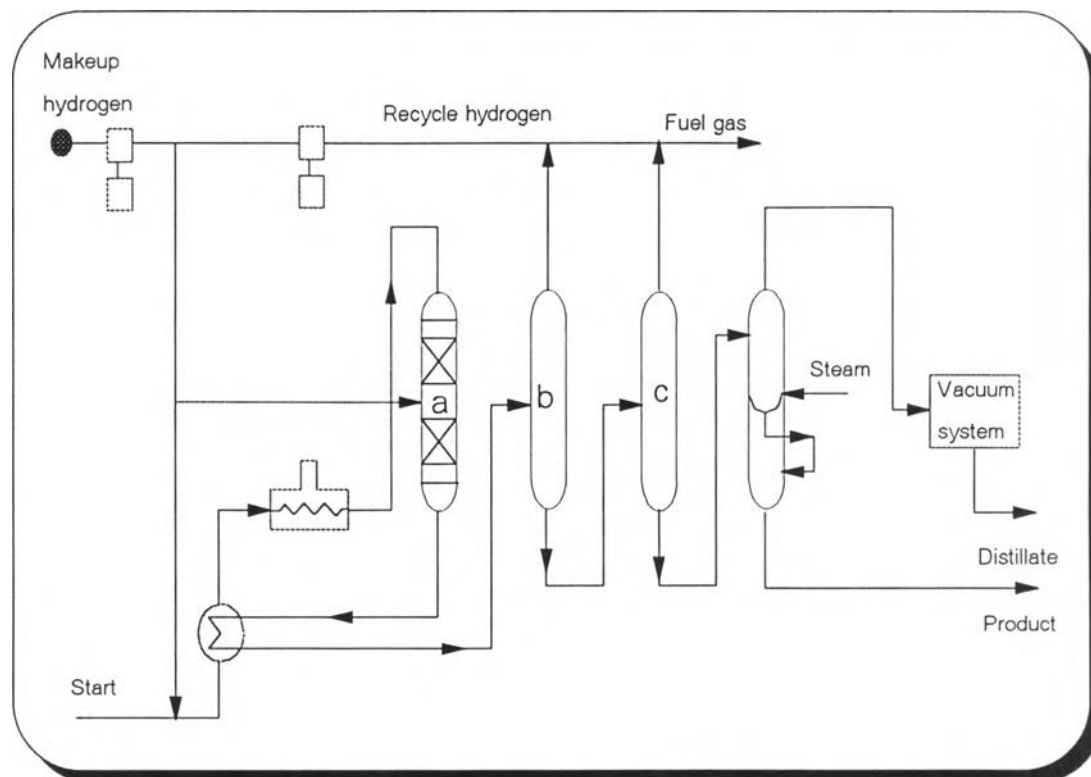


Figure 3.7 IFP Lube, wax and specialty oil hydrotreating
 a : reactor b : HP separator c : LP separator
 d : vacuum stripper / vacuum drier

Bleaching clays and bauxite are usually used for treating lubricating oils. Bauxite is sensitive toward high temperature. However, it can be regenerated by roasting after a quantity of oil is percolated which offers economic advantages.

3 Deasphalting

The highly viscous vacuum residue from vacuum distillation column oil lubricating oil contains varying amounts of asphaltenes, depending on the origin of crude oil. These components can be removed with selective solvents. In solvent refining, the raffinate is dissolved by the solvent while the asphaltenes coagulate and precipitate from the solution. The solubility of the oil in propane increases with increasing pressure and decreases with increasing temperature. The selectivity increases with temperature.

Propane Deasphalting. In propane deasphalting (Fig. 3-8) the vacuum residue is contacted countercurrently with propane. The oil solution without asphaltene is withdrawn at the tower head and the asphaltene phase at the bottom. Both streams are stripped with steam to remove the propane.

Solvent Deasphalting. Figure 3-9 shows the flow scheme of a solvent deasphalting plant with the rotating disc contactor (RDC) for the production of high quality brightstock and bitumen by the use of low-boiling liquid paraffinic hydrocarbons. The extraction efficiency can be varied by changing the rotor speed and adjusting to different throughputs. The selectivity and dissolving power of solvent can be adjusted for a desired product quality by changing the operating conditions.

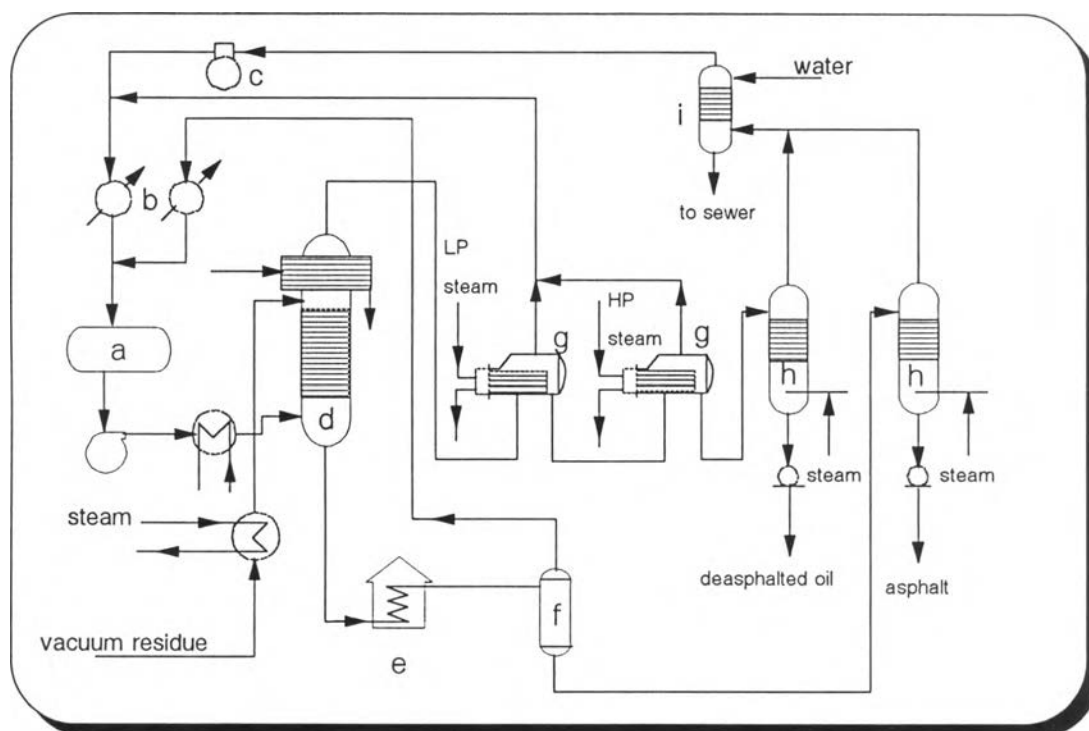


Fig. 3.8 Propane deasphalting

- a. Storage tank for propane; b. condensers; c. compressor;
- d. deasphalting column; e. furnace; f. flash drum;
- g. propane evaporator; h. strippers; i. jet condenser.

4. Dewaxing

The high melting paraffins present in Petroleum distillates give the oils high pour points, so that oil with high paraffin contents are not suited

for use as lubricating oil components. For this reason, processes have been developed at an early stage for reduction of the wax content by crystallization or extractive crystallization in order to improve low temperature properties.

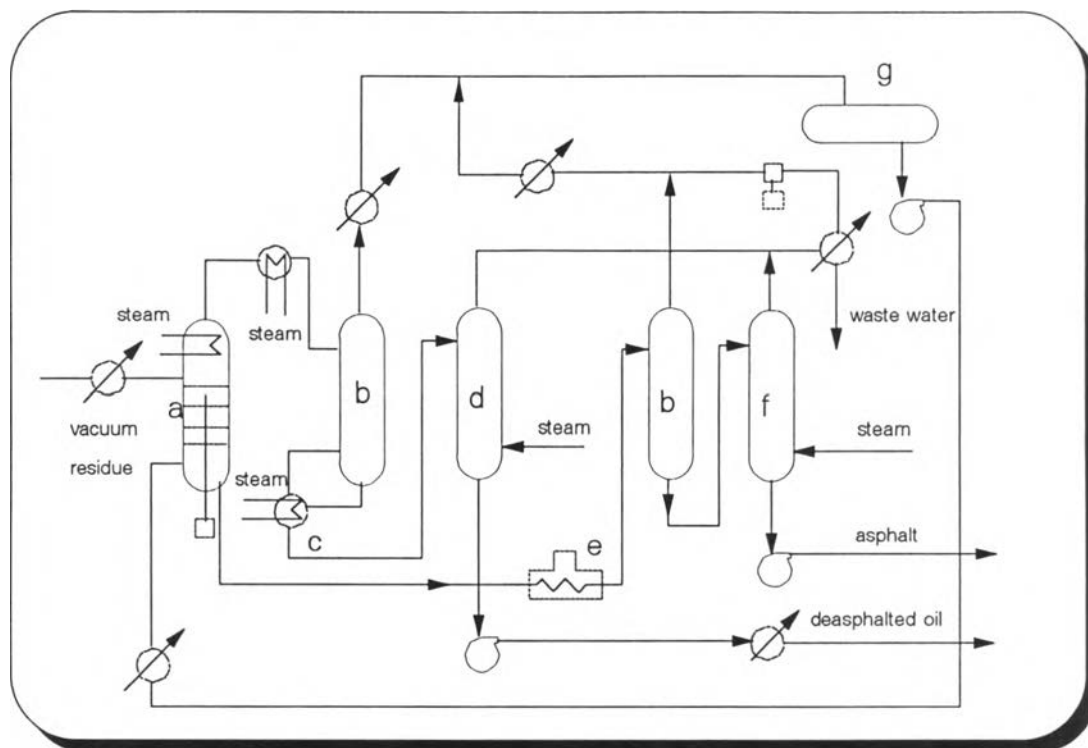


Fig. 3.9 Solvent Deasphalting

- a. Rotating - disc contactor (RDC extraction tower);
- b. flash tower; c. reboiler for deasphalted oil;
- d. deasphalted - oil stripper; e. asphalt heater;
- f. asphalt stripper; g. solvent surge drum.

The ketone-Dewaxing Process can be called the classical method. Fig. 3.11 shows a conventional ketone-dewaxer. The oil is mixed with ketone and chilled down in the scraped surface exchangers to precipitate the wax crystals. The wax is filtered off (typically at -12 C) and the solvent is recovered.

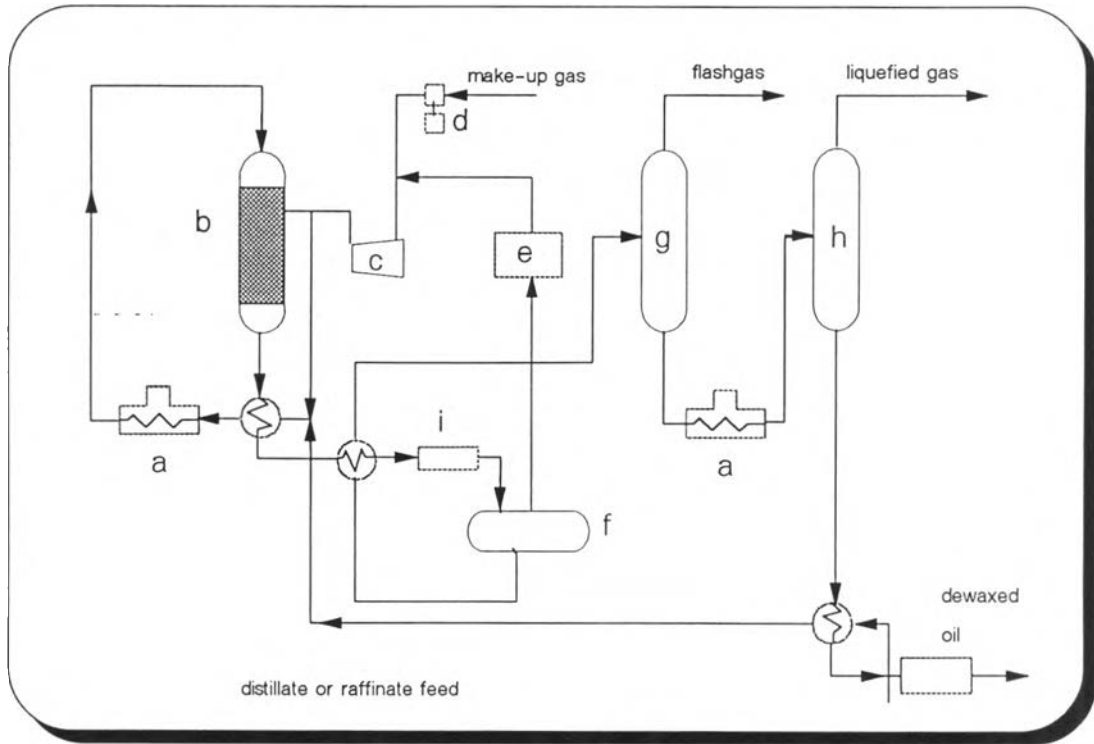


Fig. 3.10 Catalytic Dewaxing
 a. heater; b. reactor; c. recycle gas compressor;
 e. recycle gas treatment; f. high-pressure separator;
 g. low-pressure separator; h. stabilizing tower; i. cooler.

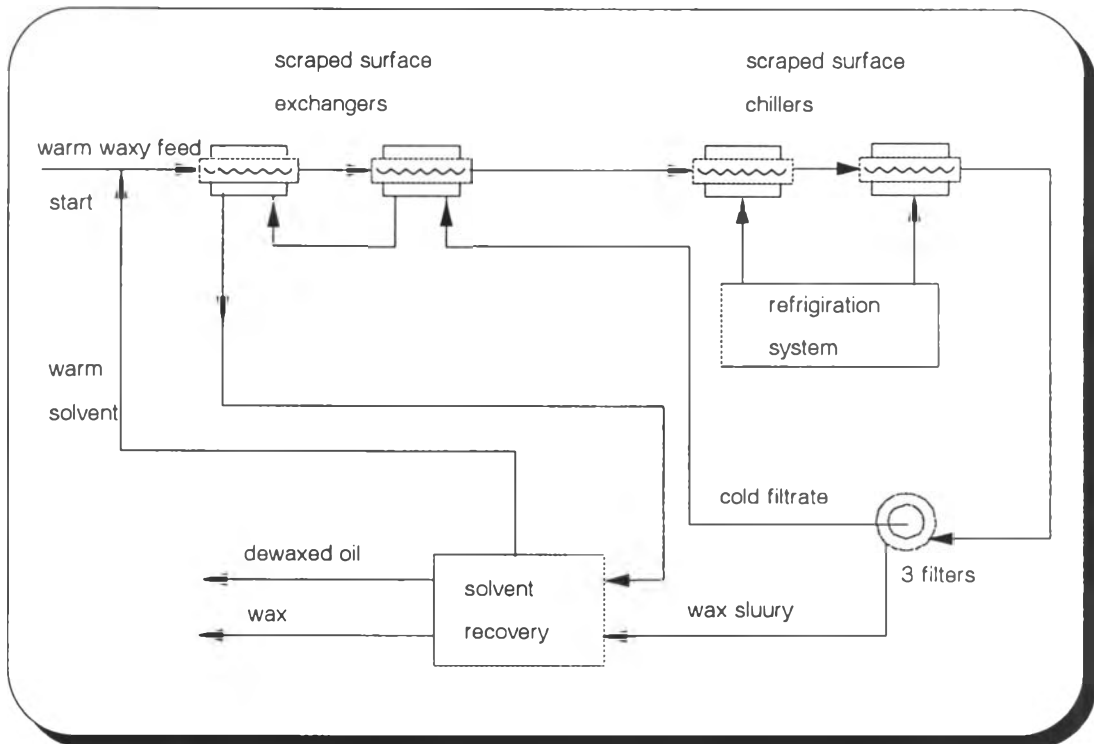


Fig. 3.11 Ketone dewaxing.

The Di-Me Solvent Dewaxing and Wax De-oiling Process was designed to prepare low pour point lubricating oils by selective crystallization of soft and hard waxes from solution of waxy oils in dichloroethane-methylene chloride mixtures (Di-Me solvent). Soft waxes can be separated from hard waxes in an optional second stage (Fig. 3.12). The warm waxy oil feed is dissolved in fresh Di-Me solvent and cooled down by heat with cold main filtrate in a shell and tube cooler and a scraped wall exchanger. Cold, oil-deficient, wash filtrate is then added to the mixture, which is then further chilled to dewaxing temperature in another scraped wall exchanger. Crystallized wax is separated from the solution in a gas-tight rotary drum filter. The main filtrate is pumped through heat exchangers to a new energy efficient solvent recovery system. The bulk of the occluded oil is removed from the wax cake on the filter drum by through washing with chilled fresh solvent fed through spray nozzles. The wash filtrate is used for feed dilution. The cake, consisting of hard and soft wax, oil and solvent, is blown off the filter surface, further diluted with wash solvent from the second-stage filter, and the "repulped" mixture is refiltered at a high temperature. Filtrate from the second-stage filter consists of a solution of soft wax, oil and solvent and the wax cake consists of hard wax and solvent.

Dichill process is a modern dewaxing process. Where crystallization is achieved by addition of a high quantity of chilled solvent and vigorous stirring. Base oils from this process have very pour point due to nearly complete removal of waxes. It can also be used to make wax with oil content less than 0.5%.

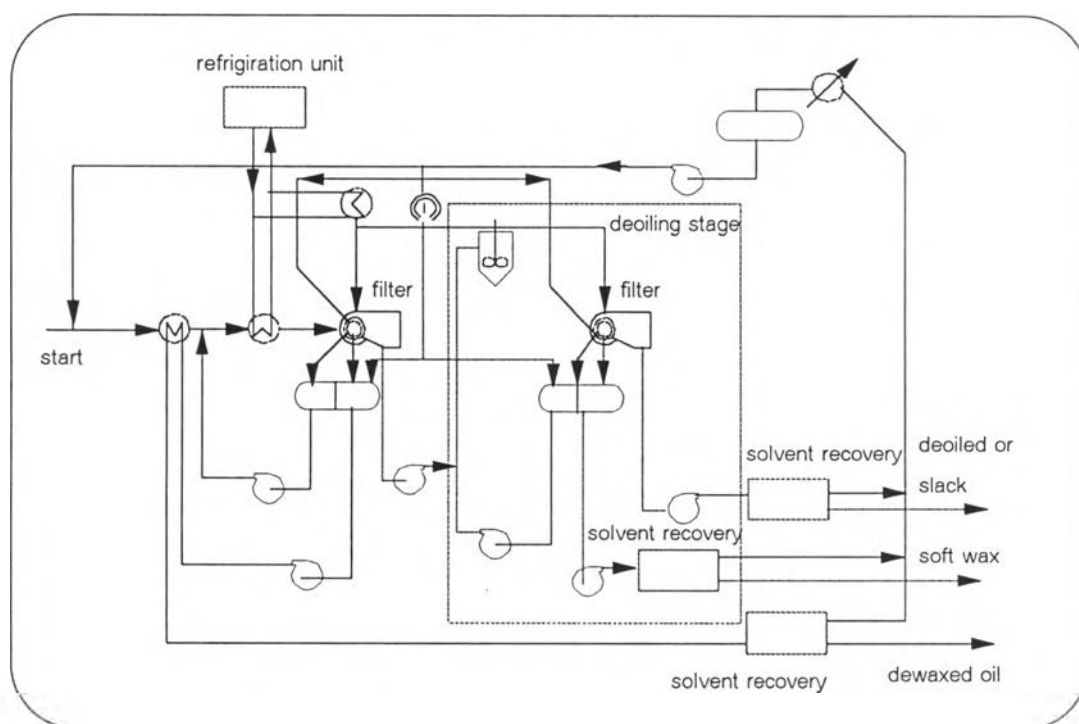


Fig. 3.12 Di-Me Solvent Dewaxing and Wax Deoiling.

Urea dewaxing is another method of wax removal. The principle of this process is that urea combines with n-paraffins forming solid inclusion compounds (adducts). Then solid adduct is separated from oil by filtration and wash with solvent. After removal of solvent by distillation, a low pour point product is obtained.

5 Hydrocracking

Hydrocracking has not been developed for the production of lubricating oil. However, under appropriate conditions it can give function which can be used for the production of lubricating oils. Under certain conditions this process can give higher viscosity index value than can be obtained from other processes at acceptable cost.

Conventional paraffinic base oils in the viscosity range of 12 cSt. at 100 C have a viscosity index of 95 to 100, hydrocracked oil can reach 120 or higher. Catalytic hydrocracking of slack waxes from dewaxing plants, followed by vacuum redistillation and MEK-dewaxing can lead to XHVI (extreme high viscosity index) oils with viscosity indexes of up to 150. Figure 3.13 shows folw scheme of hydrocracked base oils.

Percolation Process

As mentioned in section 3.1.2.4, percolation process is one of old fashsion method, apart from contact process which bleaching clay is used as adsorbent, used for finishing of lubricating base oils in the past. Bauxite is used as adsorbent for this process. Eventhough this process has almost completely been taken overby hydrofinishing process, it is still used for other applications such as reclamation of insulating oil and re-refining of used mineral based lubricating oil, etc.

Contact process for reclaiming oil make use of 200-mesh (77mesh /cm) clay and relatively high operating temperature. This process makes the most efficient use of the clay and produces a uniform product. The degree of reclaiming depends on the amount of clay used and the condition of the oil. The typical equipment , oil is introduced into a heated mixing chamber as a measured amount of clay is fed in through a hopper. The mixture of oil and clay is stirred as heat is applied, and the process continues until the desired temperature is reached. The time spent for this operation is approximately half an hour. The oil is then dropped into a tank before it is pump through a filter to remove spent clay from the oil. Types of percolation are explained in the next sections.

1. Percolation by gravity

This method makes use of gravity as hydrostatic head of a column of oil to force the oil through a column of adsorbent, such as bauxite. A typical gravity system, Fig. 3.13, Consists of three tanks on different levels. The upper tank is used as a dirty oil reservoir, the middle tank as the filter containing bauxite, and the lower tank as a blending tank for the filtered oil. The middle tank is equipped with a strainer-type bottom covered by a filter cloth supporting a 6 ft. (2 m.) bed of bauxite. A float valve controls the flow of oil from the dirty oil storage tank so that a constant head of approximately 15 ft. (5 m.) to the filter plate is provided. Once the process is started it continues inoperation with the very little attention other than periodic sampling. The output of gravity percolation is a graded one starting with overtreated oil and ending with oil in approximately the same condition as before treatment. To obtain a uniform product, blending is necessary. By this method, the oil can be treated to any desired degree. The rate of flow is slow, being about (10 gal/h)/ft² (400 L/h)/m² of filter bed area for an installation such as one described above. The slow flow rate results in long contact time with the filter medium which permits efficient use of the adsorbent.

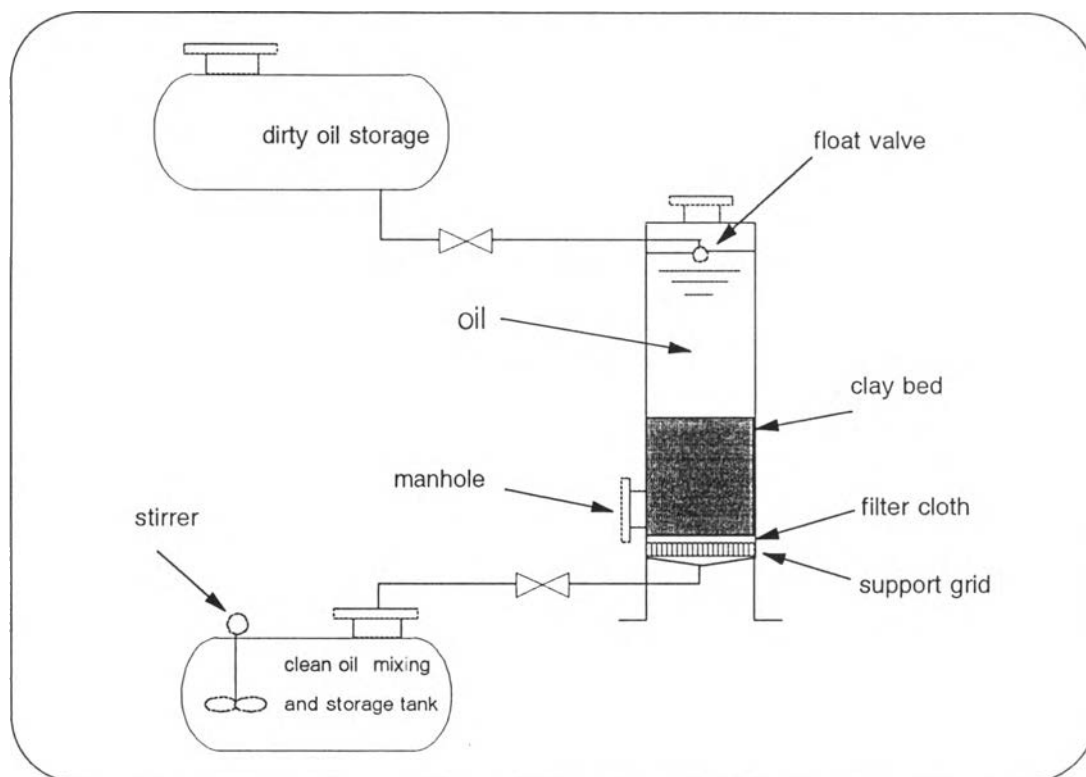


Fig. 3.13 Schematic Diagram of gravity-Percolation Refining Apparatus.

2. Percolation by Pressure

Pressure percolation similar to gravity percolation in general principle except that the oil is forced through the adsorbent by a pump. Pressure percolators are commercially available and all have a chamber to hold a container such as a bag or cartridge filled with the adsorbent. The chamber is designed so that oil is admitted around the outside of the adsorbent pack and should pass through the adsorbent before leaving the chamber.

These machines are capable of processing large volumes of oil in a relatively short time. Since the amount of adsorbent is relatively small, with respect to the amount of oil, frequent changes of adsorbent are required. An advantage of such machines is that they may be brought to the job and used directly on apparatus whose oil is to be reclaimed. The following sections explain types of pressure percolation which clay is indicated as adsorbent. Other material such as bauxite may be used.

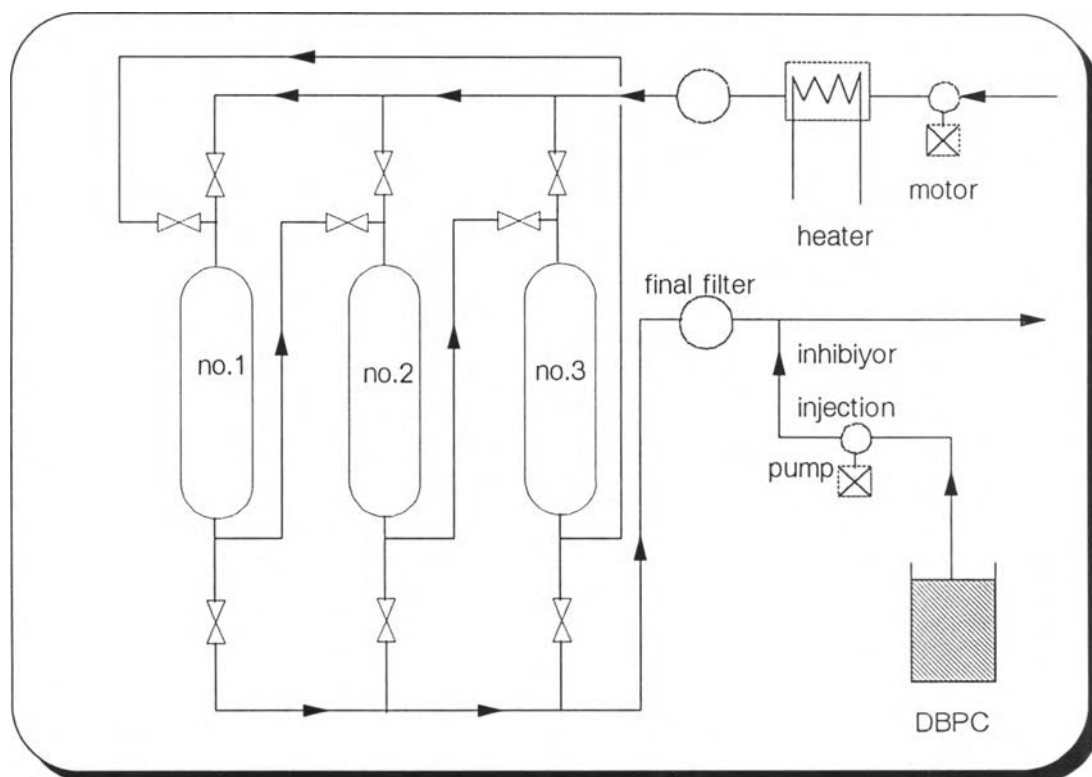


Fig. 3.15 Three-clay Tower System

2.1 Bulk filters

Large pressure tanks have a fine mesh screen across the bottom and are filled with granular clay through an open-top cover. In operation, the hot oil flows through layers of clay slowly by gravity or by pressure from an inlet oil pump. The process thus may make use of gravity or pressure percolation. See fig. 3.14.

The clay may be placed in large baskets for easy removal with a lifting device, or shoveled out through a side opening, or, in some instances, the entire pressure tank can be tilted for dumping the spent cake. The cost of operation of bulk filters is lower than that of cartridge types.

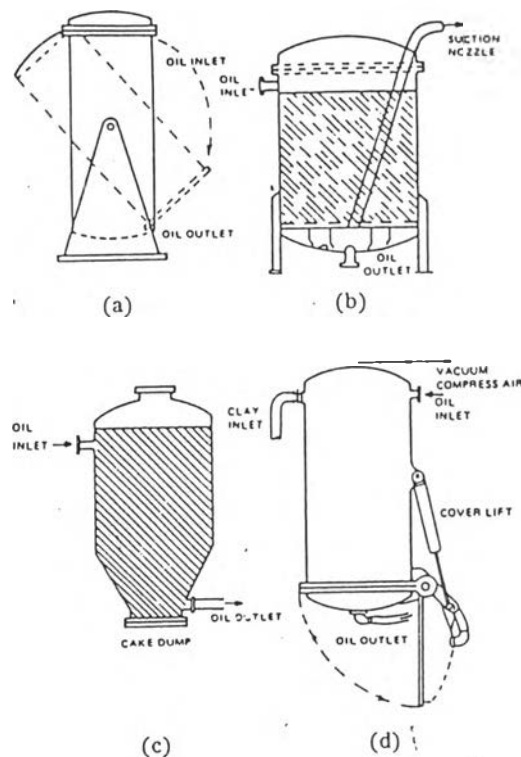


Fig. 3.14 Bulk clay filter

2.2 Deep bed filtration

Today's trend is toward slender columns packed with loose clay by means of vacuum or conveyors with spent cake discharged through a bottom opening cover. This design ensures long contact time of oil flowing from top to bottom, minimizes channeling, and provides the greatest improvement of oil conditions in a single pass. Two or three such column or towers, piped in series, provide for a better utilization of clay (Fig. 3.15). Only the first tower in series is replaced with new clay and switched into the final tower position. In this manner, an almost continuous run with a consis-

tent quality of effluent can be obtained. Each tower contains from 500 lb. to 3000 lb. of clay. Even a mobile operation, the tanks contain 200 lb - 1000 lb each.

2.3 Throw - Away and Repackable cartridges.

Granular types of clay are repackaged in throw-away canisters, holding 10 lb - 30 lb of material, which are placed inside pressure-filter tanks. Protective antimigration filter cloth wrap is either inside the element or wrapped around the center tube. See Fig. 3.16. Throw-away cartridges and canisters are relatively expensive and can be justified only in emergencies or when a marginal condition of the oil requires removal of a trace contaminant. The limited amount of clay can not be effective on very contaminated oil.

Repackable cartridge or canisters are less costly and are usually of a large size, holding as much as 50 lb or more of clay each. After use, the canisters are removed and the clay replaced with new, dry material. In most cases this is more economical than the throw-away cartridge.

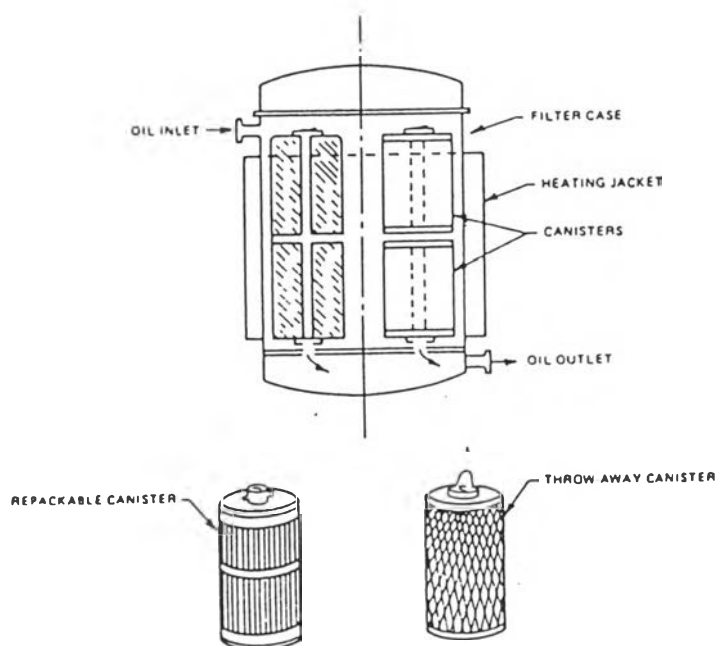


Figure 3.16 Fuller's Earth Cartridge Filter

2.4 Percolation by thermo-Siphon By pass.

Good oil that is deteriorating slowly may be held in safe operating condition by applying a special bypass earth filter to the individual transformer either on new equipment or added later. The oil is forced through the filter by the action of the heat generated by the apparatus and the heat dissipated by the filter.

The bypass method of maintaining oil in usable condition has certain definite limitations. On standby transformers or on circuit breakers it is in operative since the heat necessary to its operation is not constantly available. The operation of bypass filters might also be termed very gentle since little force is available to drive the oil through even a coarse filter bed. There is also the possibility that fine particles of the earth may leak through the system into the processed oil. The adsorbents shall be changed regularly.

3 Bauxite

Bauxite is a natural aggregate of aluminum-bearing minerals, more or less impure, in which the aluminum occurs largely as hydrated oxides. It is usually formed by prolonged weathering of aluminous rocks. Bauxite contains 30-75% Al_2O_3 , 9-31% H_2O , 3-25% Fe_2O_3 , 2-9% SiO_2 and 1-3% TiO_2 . It is a nontoxic and noncombustible substance. Color of bauxite can be different, white cream, yellow, brown, gray or red, depending on its origin. The origins of bauxite are Australia, Jamaica, France, Guiana, Guinea, U.S. (Arkansas) and Brazil. Bauxite has specific gravity between 2-2.55 and Mohs hardness between 1-3. It is insoluble in water and can be decomposed by hydrochloric acid. As mentioned about the uses of bauxite in previous section it is also used as decolorizing and deodorizing agent, catalysis, filler in rubber, plastics, paints and cosmetics, and hydrolic fracturing.